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Energy translation operator

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An operator is defined that is analogous to the time translation operator except that it translates every component of a state in energy by an amount ε . A prescription for measuring expectation values of this operator is described. These measurements provide phase information that is not obtainable by other means. The similarity of this treatment with the treatment of recurrence spectroscopy in the time domain is presented. Two examples from atomic systems are described, but the usefulness of this operator is not restricted to atomic processes. [S1050-2947(97)03111-9]

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The properties of quantum systems (e.g., atoms, molecules, nuclei, and solids) have typically been explored by measuring the response of the system to a monochromatic driving field. This response depends on the squared amplitude for the process to occur at that frequency summed over all of the indistinguishable final states of the process. The response depends on the initial state of the system and on the states of the system at an energy $\hbar\omega$ above (or sometimes below) the initial-state energy. For example, if an atom is in an initial state, the photoionization cross section is proportional to $\sum_j d_{E_j}^- d_{E_j}^{*-}$, where the j index the ionization channels and the excitation amplitude depends on the dipole matrix element coupling the initial state to the energy-normalized final states. Of course, all phase information is lost in this type of measurement; thus it is impossible to predict the detailed response of the system to a pulsed driving field from this type of measurement. However, some time-dependent information is available. Recent work has shown that by Fourier transforming the energy-dependent response, an expectation value of the time translation operator may be obtained. This is an overlap between a state of the system at time 0 with itself at time t [1]. This overlap can also be measured directly [2–9].

The response of quantum systems to a pulsed driving field recently has been measured directly through the generation and detection of wave-packets [2–22]. (To avoid giving the large list of fruitful wave packet experiments, I will focus on electron wave packets. It must be remembered, though, that every aspect of this paper applies equally well to other types of time-dependent quantum measurements [11].) In these studies, the initial state is a superposition of many different energy components. Typically, the behavior of an electron wave packet is probed by measuring the time-dependent probability for it to be in the vicinity of the nucleus [12–16] or by measuring the time-dependent flux of electrons ejected

from autoionizing states [17–21]. It is also possible to measure components of the momentum distribution [22]. The purpose of these studies is to observe the time evolution of quantum systems since this is more analogous to our experience with classical phenomena. It also provides us with a fuller understanding of the quantum systems by forcing us to view the system in the time domain.

It is the purpose of this paper to answer the following question: What is obtained when the time-dependent measurements are Fourier transformed? The question appears pointless because this Fourier transform is going to give some sort of energy information and the whole point of time-dependent measurements is to get away from the energy domain. It is shown below that what is obtained is the expectation value of an energy translation operator. Further, it is shown that the information thus obtained cannot be measured using the more typical energy-dependent response of the system to the field. Relative phase information between different energy-states may be obtained. These measurements are not restricted to atomic systems, although both examples given in this paper are for atomic processes: *measuring* the increase of phase through a resonance and *measuring* the change in sign of the dipole matrix element across a Cooper minimum.

The energy translation operator will be discussed within the context of a specific experimental arrangement. Recent experiments [17,20] measured the time-dependent flux $I(t)$ of electrons into a detector a distance r_0 from an atom in a static electric field. The initial state of the atom is created by exciting it to energies above the classical ionization threshold but below the zero-field threshold using a weak, pulsed laser that has a full width at half maximum (FWHM) of a few picoseconds. To discover the physical interpretation of the Fourier transform of $I(t)$, it is necessary to have a theoretical description of this parameter.

The theoretical description of this process is simplest when using the outgoing-wave-type continuum wave functions ψ_{Ej}^- ; this function only has outgoing waves in channel j and incoming waves in all other channels. These functions are energy normalized $\langle \psi_{Ej}^- | \psi_{E'j'}^- \rangle = \delta_{jj'} \delta(E - E')$ and an unusual phase convention is employed $\psi_{Ej}^- = \exp[-i\phi_j(r_0)] \tilde{\psi}_{Ej}^-$, where the $\tilde{\psi}_{Ej}^-$ are the more usual outgoing-wave solutions and $\phi_j(r_0)$ is the phase accumulation in channel j from the nucleus to the detector $\text{Im}\{\ln[f_j^+(r_0)]\}$ (f_j^+ is the outgoing wave in channel j). If the laser pulse has amplitude $A(E)$ for containing a photon to excite the atom to energy E , then the wave function at the detector is

$$\psi(\vec{r}_0, t) = \int dE \sum_j \Phi_j(\Omega) A(E) \langle \psi_{Ej}^- | T | \psi_g \rangle e^{-iEt}, \quad (1)$$

where $\Phi_j(\Omega)$ is the function for all the degrees of freedom of the system orthogonal to the direction of motion of the electron and T is the transition operator that is proportional to x , y , or z depending on the polarization.

The flux into the detector is proportional to $|\psi|^2$ integrated over the transverse modes

$$I(t) = K \int dE \int dE' \sum_j \langle \psi_g | T | \psi_{E'j}^- \rangle A^*(E') e^{i(E' - E)t} A(E) \times \langle \psi_{Ej}^- | T | \psi_g \rangle, \quad (2)$$

where K is the proportionality constant and I have neglected the different velocities in the different channels. For atoms in electric fields, the electrons have the same speed in all channels; for atoms in zero field, the different times of flight in the different channels separate the pulses by such large times that it is unlikely they would be measured in the same experiment.

The Fourier transform of the flux can be obtained in a rather trivial manner

$$\begin{aligned} \eta(\varepsilon) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} I(t) e^{-i\varepsilon t} dt \\ &= K \int dE \sum_j \langle \psi_g | T | \psi_{E+\varepsilon, j}^- \rangle A^*(E + \varepsilon) A(E) \\ &\quad \times \langle \psi_{Ej}^- | T | \psi_g \rangle, \end{aligned} \quad (3)$$

with $\varepsilon \geq 0$ by definition. What is the meaning or physical idea in this equation? This equation can be interpreted using as the definition of a state $|\Psi\rangle = A(H)T|\psi_g\rangle\sqrt{K}$, where H is the Hamiltonian of the system; this function has the energy representation

$$|\Psi\rangle = \sqrt{K} \int dE \sum_j |\psi_{Ej}^- \rangle A(E) \langle \psi_{Ej}^- | T | \psi_g \rangle. \quad (4)$$

With these definitions the Fourier transform of the flux is equal to

$$\eta(\varepsilon) = \langle \Psi | W(\varepsilon) | \Psi \rangle, \quad (5)$$

where $W(\varepsilon)$ is the operator

$$W(\varepsilon) = \int dE \sum_j |\psi_{E+\varepsilon, j}^- \rangle \langle \psi_{Ej}^-|. \quad (6)$$

To interpret this operator, note the relations

$$W(\varepsilon) |\psi_{Ej}^- \rangle = |\psi_{E+\varepsilon, j}^- \rangle, \quad (7)$$

$$W(\varepsilon_1) W(\varepsilon_2) = W(\varepsilon_1 + \varepsilon_2), \quad (8)$$

$$W(\varepsilon) W^\dagger(\varepsilon) = 1, \quad (9)$$

$$W^\dagger(\varepsilon) W(\varepsilon) \neq 1. \quad (10)$$

Relations (7)–(9) indicate that the $W(\varepsilon)$ operator behaves as an energy translation operator. Relation (10) shows that the similarity to the time translation operator is not complete. The reason $W^\dagger W \neq 1$ is because the number of channels increases with increasing energy.

Before continuing the discussion of the energy translation operator, the method for obtaining the expectation value of $W(\varepsilon)$ should be compared with the method for obtaining the expectation value of the time translation operator. Take the energy-dependent response $R(E) = K \sum_j |\langle \psi_{Ej}^- | T | \psi_g \rangle|^2$, multiply by $|A(E)|^2$, and then Fourier transform. The resulting function of time is

$$\begin{aligned} \rho(t) &= \int_{-\infty}^{\infty} R(E) |A(E)|^2 e^{-iEt} dE \\ &= \langle \Psi | U(t) | \Psi \rangle, \end{aligned} \quad (11)$$

where $|\Psi\rangle = A(H)T|\psi_g\rangle\sqrt{K}$ and $U(t) = \exp(-iHt)$ is the time translation operator. From this, the similarity between the two operators U and W is apparent. The basic similarity consists in the identification of $\rho(t)$ as a overlap between a state and itself, but where every component has been shifted forward in time by an amount t ; $\eta(\varepsilon)$ can be identified as an overlap between a state and itself, but where every component has been shifted in energy by an amount ε : $\eta(\varepsilon) = \int dE \sum_j C_{E, j} C_{E+\varepsilon, j}^*$. An interesting point is that with the current definitions $\rho(0) = \eta(0)$ if $A(E)$ is the same in ρ and η and K is the same in ρ and η .

However, beyond this one point, $\varepsilon = 0$, it is *impossible* to obtain the $\eta(\varepsilon)$ function from the energy-dependent response function. This is because the $\eta(\varepsilon)$ function depends on the relative phase of the dipole matrix elements between states separated in energy by an amount ε . From the preceding derivation, it is clear that the expectation value of $W(\varepsilon)$ is a measurable quantity, but perhaps it is not clear that it is a quantity worth measuring. After all, the reason for doing wave packet studies is that you can make quantum systems behave somewhat classically. The important point is that there is phase information available in $\eta(\varepsilon)$ that is not obtainable in principle from $R(E)$. In certain interesting circumstances it allows the measurement of the relative phase dependence of the wave function. Below two interesting examples of this possibility are given.

The first interesting case involves the behavior of $\eta(\varepsilon)$ near two resonances, one that is much sharper than the other. To be specific, the transition amplitudes will have the form

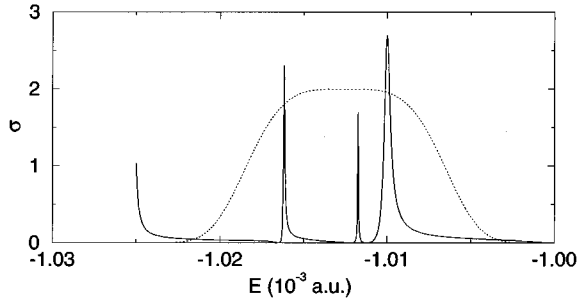


FIG. 1. Solid line, proportional to the ground-state infinite resolution photoionization cross section (in arbitrary units) of Na in a static electric field as a function of the electron's energy $F_{\text{stat}}=1990$ V/cm and the laser polarized perpendicular to the static electric field; dotted line; proportional to $A(E)$, the amplitude for finding a photon at each energy.

$$\langle \psi_{E_j}^- | T | \psi_g \rangle = T_{c_j} + \frac{T_{1j}}{E - E_1 + i\Gamma_1/2} + \frac{T_{2j}}{E - E_2 + i\Gamma_2/2}, \quad (12)$$

where T_{c_j} , T_{1j} , and T_{2j} are essentially energy independent and E_i, Γ_i are the position and width of the two resonances. To be specific, we choose $E_1 < E_2$ and $\Gamma_1 \ll \Gamma_2$ (i.e., the lower-energy resonance is the sharper one). If either $T_{1j} \gg T_{2j}$ or $E_2 - E_1 > \Gamma_2$, the excitation amplitude can be chosen in such a way that

$$\begin{aligned} \eta(\varepsilon) &\propto \sum_j \left(T_{c_j}^* + \frac{T_{2j}^*}{E_1 + \varepsilon - E_2 - i(\Gamma_1 + \Gamma_2)/2} \right) T_{1j} \\ &\approx \sum_j \langle \psi_g | T | \psi_{E_1 + \varepsilon}^- \rangle T_{1j} \end{aligned} \quad (13)$$

for $\varepsilon \gg \Gamma_1$. This allows the measurement of the complex conjugate of the dipole matrix elements dotted into the amplitude for exciting resonance 1.

In Fig. 1 the ground-state total photoionization cross section for Na in a 1990-V/cm static field is shown for a laser polarized perpendicular to the static field direction. This was calculated using the method described in Ref. [21]. The dashed line is the $A(E)$ used to excite the wave packet. There are three resonances excited by this pulse at energies -1.01618×10^{-3} , -1.01174×10^{-3} , and -1.01000×10^{-3} a.u. These resonances have asymmetric profiles due to the interference between the resonant and direct amplitudes. In Fig. 2 the imaginary part of $\eta(\varepsilon)$ versus its real part for the case shown in Fig. 1 is plotted. No approximations were made in this calculation except the numerical approximations inherent in the calculation of the dipole matrix elements. The following points in ε are marked: (i) $\varepsilon = 3.63 \times 10^{-6}$ (diamond), the smallest value of ε in this plot; (ii) $\varepsilon = 4.44 \times 10^{-6}$ (triangle), the exact spacing between the lowest two resonances; (iii) $\varepsilon = 5.93 \times 10^{-6}$ (square), the spacing between the lowest and highest resonances minus the halfwidth of the highest resonance. (iv) $\varepsilon = 6.18 \times 10^{-6}$ (cross), the exact spacing between the lowest and highest resonances; and (v) $\varepsilon = 6.47 \times 10^{-6}$ (plus), the spacing between the lowest and highest resonances plus the halfwidth of the highest resonance.

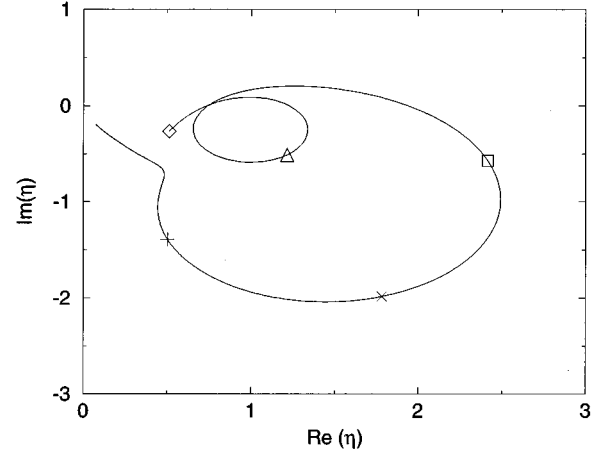


FIG. 2. Imaginary part of $\eta(\varepsilon)$ plotted versus the real part. The symbols on the line are particular values of ε as discussed in the text. η is in arbitrary units.

There are several interesting features of this plot that can be understood from the approximate equation (13). (i) As ε becomes nearly equal to the spacing of two resonances, the trajectory of $\eta(\varepsilon)$ in the complex plane approximately executes an elliptical-type motion. (The initial value of ε is too large to see the third ellipse that arises when ε equals the difference in energy of the middle and upper resonances.) The eccentricity of the ellipse depends on the asymmetry of the broader resonance: Lorentzian resonances produce circles and window resonances produce straight lines. (ii) The trajectory of $\eta(\varepsilon)$ traverses the ellipse in a clockwise direction. (iii) Not shown on the figure is that $d\eta/d\varepsilon$ is largest at the triangle and cross (i.e., when ε equals the spacing of two resonances); the rate of phase change is largest on resonance. (iv) The diameter of the ellipse is related to the product of the oscillator strength of the two resonances separated by energy ε (i.e., the larger the oscillator strength of the resonance, the larger the ellipse).

It is clear from Fig. 2 that the phase of η decreases by 2π as ε is varied over each of the resonance spacings. In particular, the trajectory for the region of ε near the energy difference of the lowest and highest resonances follows the form predicted by Eq. (13). (As an aside, one π of this phase comes from the phase shift of the continuum wave and the extra π of this phase arises from the energy-dependent amplitude multiplying the autoionizing resonance part of the wave function.) This example shows that it is possible to measure the change in phase of the dipole matrix element across a resonance.

Another interesting case involves the change in sign of the dipole matrix element across a Cooper minimum in the photoionization cross section. If the minimum is at a high enough energy, the dispersion of the electron wave traveling to the detector can be neglected. A wave packet created with the main photon frequency centered on the Cooper minimum will give information on the sign change of the dipole matrix element if ε is chosen large enough so that the correlation function of the dipole matrix element $T_E^* T_{E+\varepsilon}$ involves energies from opposite sides of the Cooper minimum.

A simpler experiment to measure the sign change across a Cooper minimum can use the system discussed in Ref. [23].

A wave packet around a Cooper minimum in the bound-state region can be created in Li. In this situation, the wave function is given by

$$\psi(\vec{r}, t) = \sum_n C_n(t) d_n e^{-iE_n t} \psi_n(\vec{r}), \quad (14)$$

where

$$C_n(t) = -i \int_{-\infty}^t F(t') e^{i(E_n - E_g - \omega)t'} dt' \quad (15)$$

and $d_n = (E_n - E_c)D/(n - \mu)^{3/2}$, with $F(t)$ the laser field amplitude, D a constant, and μ the quantum defect; the quantity E_c is the energy at which the dipole matrix element changes sign. $C_n(t)$ quickly approaches $A(E_n)$ as t gets larger than the FWHM of the pulse. In a pump-probe experiment where a second laser excites the wave packet into the continuum, measuring the probability for ionization versus the time delay between pulses gives $|\psi(0, t)|^2$ to a good approximation since the electron absorbs photons most efficiently when it is near the nucleus. This simplifies the calculation because each component of the wave function behaves like $\psi_n(\vec{r}) \approx F(\vec{r})/(n - \mu)^{3/2}$ near the nucleus. Fourier transforming this quantity with a small imaginary part to ε gives

$$\begin{aligned} \eta(\varepsilon - i\delta/2) &= \frac{-iK}{\pi} \sum_{n, n'} A(E_n) A^*(E_{n'}) \\ &\times d_n d_{n'}^* / [(v\nu')^{3/2} (E_n + \varepsilon - E_{n'} - i\delta/2)], \end{aligned} \quad (16)$$

where $\nu = n - \mu$. If δ is chosen to be much smaller than the difference in energy spacings, the η function can be inte-

grated over one of the peaks to give

$$\int_{E_n' - E_n - 10\delta}^{E_n' - E_n + 10\delta} \eta(\varepsilon - i\delta/2) \approx KA(E_n)A^*(E_{n'})d_n d_{n'}^* / (v\nu')^{3/2}. \quad (17)$$

This lets one *measure* the sign change of the dipole matrix elements because if n and n' are such that $E_n < E_{n'} < E_c$ or $E_c < E_n < E_{n'}$, then the parameter in Eq. (17) should be positive. If $E_n < E_c < E_{n'}$, then the parameter should be negative.

These two examples show that the energy translation operator could be a powerful tool for measuring previously undetectable parameters. A more concerted effort will be needed to understand the behavior of the energy translation operator in more complex circumstances. A couple of examples that might show interesting behavior will suffice. First-row atoms and many molecular systems have ionization thresholds that have a small spacing; an electron wave packet in these systems will give radial motion for the electron as well as for the core that remains after the electron is kicked out; interesting correlations are expected when ε is chosen to equal the core energy spacing. Rydberg states that are subject to unidirectional kicks by a pulsed electric field evolve like a wave packet; contrasting the correlation in these states to those created from pulsed lasers may shed light on the dynamics. Wave packets constructed from states in static electric or magnetic fields are difficult to understand due to the interactions between nearly degenerate states; by giving relative signs of dipole matrix elements and correlations between states at different energies the energy shift operator may provide another method for unraveling the quantum dynamics.

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- [1] R. Schinke, *Photodissociation Dynamics* (Cambridge University Press, Cambridge, 1993).
- [2] L. D. Noordam, D. I. Duncan, and T. F. Gallagher, *Phys. Rev. A* **45**, 4734 (1992).
- [3] R. R. Jones, C. S. Raman, D. W. Schumacher, and P. H. Bucksbaum, *Phys. Rev. Lett.* **71**, 2575 (1993).
- [4] B. Broers, J. F. Christian, J. H. Hoogenraad, W. J. van der Zande, H. B. van Linden van den Heuvell, and L. D. Noordam, *Phys. Rev. Lett.* **71**, 344 (1993).
- [5] Q. Wang and A. F. Starace, *Phys. Rev. A* **48**, R1741 (1993).
- [6] B. Broers, J. F. Christian, and H. B. van Linden van den Heuvell, *Phys. Rev. A* **49**, 2498 (1994).
- [7] L. Marmet, H. Feld, G. Raithel, J. A. Yeazell, and H. Walther, *Phys. Rev. Lett.* **72**, 3779 (1994).
- [8] I. Y. Kiyan and D. J. Larson, *Phys. Rev. Lett.* **73**, 943 (1994).
- [9] H. H. Fielding, J. Wals, W. J. van der Zande, and H. B. van Linden van den Heuvell, *Phys. Rev. A* **51**, 611 (1995).
- [10] I. Sh. Averbukh and N. F. Perel'man, *Usp. Fiz. Nauk.* **41**, 161 (1991) [*Sov. Phys. Usp.* **34**, 572 (1991)].
- [11] A. H. Zewail, *Femtochemistry* (World Scientific, Singapore, 1994).
- [12] A. ten Wolde, L. D. Noordam, A. Lagendijk, and H. B. van Linden van den Heuvell, *Phys. Rev. A* **40**, 485 (1989).
- [13] J. A. Yeazell and C. R. Stroud, *Phys. Rev. Lett.* **60**, 1494 (1988); J. A. Yeazell, M. Mallalieu, J. Parker, and C. R. Stroud, *Phys. Rev. A* **40**, 5040 (1989).
- [14] X. Wang and W. E. Cooke, *Phys. Rev. Lett.* **67**, 1496 (1991); *Phys. Rev. A* **46**, 4347 (1992).
- [15] D. W. Schumacher, D. I. Duncan, R. R. Jones, and T. F. Gallagher, *J. Phys. B* **29**, L397 (1996).
- [16] D. I. Duncan and R. R. Jones, *Phys. Rev. A* **53**, 4338 (1996).
- [17] G. M. Lankhuijzen and L. D. Noordam, *Phys. Rev. Lett.* **76**, 1784 (1996).
- [18] F. Robicheaux and W. T. Hill III, *Phys. Rev. A* **54**, 3276 (1996).
- [19] F. Robicheaux and J. Shaw, *Phys. Rev. Lett.* **77**, 4154 (1996).
- [20] G. M. Lankhuijzen, F. Robicheaux, and L. D. Noordam, *Phys. Rev. Lett.* (to be published).
- [21] F. Robicheaux and J. Shaw, *Phys. Rev. A* **56**, 278 (1997).
- [22] R. R. Jones, *Phys. Rev. Lett.* **76**, 3927 (1996).
- [23] J. Hoogenraad, R. B. Vrijen, and L. D. Noordam (unpublished).